Synopsis of the thesis titled

Studies on Structural, Dielectric, Magnetic, Ferroelectric and Magnetoelectric Properties of (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ Particulate Composites

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1. Introduction & Review of Literature

In recent years, there has been increasing interest on the multiferroic magnetoelectric composites because of their great potential for use in a wide range of technological applications such as magnetic field sensors, transducers, filters, oscillators, phase shifters and multi-state memory devices [1-4]. These composite materials exhibit simultaneous ferroelectric, ferromagnetic behaviour as well as magnetoelectric coupling effect which could lead to several technological advantages and fascinating physics over traditional magnetic and ferroelectric materials. For example, the coupling of magnetization and electrical polarization could in principle allow data to be written electrically and read magnetically (a new type of memory), thus overcome the difficulties associated with reading ferroelectric random access memory (fatigue) and requiring large magnetic field (high Hc) to write magnetic data storage [5]. There are limited numbers of naturally existing single-phase multiferroic magnetoelectric materials due to the fact that ferromagnetism and ferroelectricity are often incompatible as one requires empty d-orbitals while the other expects them to be partially filled [6-7]. The naturally occurring single-phase multiferroics such as $RMnO_3$, RMn_2O_5 (R = rare earth, Y, and Bi), exhibit ferroic properties either at low temperatures or their magnetoelectric responses are very weak. This has hampered device-driven progress and focus is being directed towards exploring artificial multiferroics. Accordingly, artificial multiferroic systems including doping of transition metals in ferroelectrics, multilayer and bulk composites of a ferromagnet (or ferrimagnet) and a ferroelectric have been extensively studied during the last few years. It has been observed that composite type magnetoelectric multiferroics made by combining piezoelectric and magnetic phases yield a large magnetoelectric (ME) response of several orders of magnitude higher than that in those single phase compounds even above room temperature. It was also recognized that composite materials showed the potential for engineering new multiferroic magnetoelectric materials having desirable properties that are not found in single phase materials [8-10]. In multiferroic magnetoelectric composites, the coupling interaction between the magnetic and electric order parameters could produce new effect, which is termed as magnetoelectric (ME) effect. The ME effect is defined as an induced electric polarization (P) of a material with an applied magnetic field (H), i.e., direct effect or an induced magnetization (M) with an external electric field (E), i.e., converse effect.

$$\text{Direct ME effect, } \Delta E = \alpha_E \Delta H \quad (1)$$

$$\text{Converse ME effect, } \Delta M = \alpha \Delta E \quad (2)$$

Where, $\alpha(\alpha_E)$ is the ME voltage coefficient. This means that electric polarization and magnetization can be modified by the application of a magnetic field and electric field of the

materials via the ME coupling [11-12]. Composite magnetoelectrics are combinations of magnetostrictive and electrostrictive materials, such as ferromagnetic and piezoelectric materials. The ME effect in composite system is that the magnetic field induced strain in the magnetostrictive component which is transferred to piezoelectric component through elastic coupling exhibit electric polarization or vice versa. Thus, ME effect in composite materials is known as a product tensor property which results from the cross interaction between the different ordering of two phases in composites. When magnetic field is applied to a composite material the magnetic phase changes its shape magnetostrictively and strain is passed along to the piezoelectric phase exhibiting an electric polarization. The ME effect in composites is extrinsic property depending upon the composite microstructure and coupling interaction between magnetic and piezoelectric interfaces. In single phase magnetoelectrics the effect can be due to the coupling of magnetic and electric orders as observed in some multiferroics, while in composite materials the effect originates from interface coupling effects, such as strain. These ME composites have potential applications as multifunctional devices such as magnetic field sensors, magnetoelectric gyrators and microwave devices etc [13]. The strain coupling occurs from intimate contact between the constituent phases and depends strongly on the geometry of the connectivity of the phases. The geometry of two phase composites are described by notations 0-3, 2-2, 1-3 etc as introduced by Newnham [14], where each number denotes the connectivity of each phase. For example, 0-3 particulate composite means single phase particles denoted by 0 dispersed in a matrix of another phase denoted by 3. There are some important issues for successful preparation of high quality composites include chemical reaction between ferroelectric and ferromagnetic phases in the composites during processing should be kept as minimum as possible, the defects at the interfaces of two phases should be avoided to achieve substantial mechanical coupling in the composites and uniform dispersion of two phases to enhance the electric resistivity of the composites. In fact, when the ferromagnetic phase in the composites connects in chainlike manner, the electric resistivity is significantly reduced. Thus, it is utmost important to disperse the ferromagnetic phase uniformly in the composites. The research interest in multiferroic magnetoelectric composites is to enhance the coupling effect.

The existing literature survey reveals that there is an enormous research work that is going on various ceramic composites with different connectivity scheme including 0-3-type particulate composites and 2-2-type laminate composites for the enhancement of ME coupling effect. The first work on ME composites done by Van Suchtelen [15] and prepared ME composites by unidirectional solidification of a eutectic composition of the Fe-Co-Ti-Ba-O and have obtained a ME voltage coefficient dE/dH=130mV/cmOe which is higher than single phase materials. A large number of ME particulate ceramic composites have been developed that mainly consist of Pb(Zr,

Ti)O_3 (PZT), $BaTiO_3$, or $BiFeO_3$ as piezoelectric/ferroelectric phases with $NiFe_2O_4$, $CoFe_2O_4$ as magnetic phases [16-21]. Thus, in order to maximize the ME coupling in the composites it is desirable to incorporate a ferromagnetic phase having a large magnetostriction coefficient, a ferroelectric component with a large piezoelectric response, and enhance the mechanical coupling between the two phases. Among various piezoelectric materials, Ca modified $PbTiO_3$, especially $(Pb_{0.70}Ca_{0.30})TiO_3$ (PCT) could be another promising choice for piezoelectric constituent in multiferroic ME composite because of its large piezoelectric response [22-23]. On other hand $CoFe_2O_4$ (CFO) is well known magnetostrictive due to its highest value of negative saturation magnetostriction ($\lambda \sim - 252 \times 10^{-6}$) with a moderate magnetization (Ms ~ 81emu/g), good chemical stability and significant hardness while low ME voltage coefficients ~ 5-6 mV/cm Oe have been reported for $PbZr_{0.52}Ti_{0.48}O_3$-$CoFe_2O_4$ composites [24-25]. The low ME voltage coefficient in CFO based composites arises due to its large magnetic anisotropy and high coercivity that restricts the domain wall dynamics. Nevertheless, the substitution of Fe by Mn at octahedral site B in CFO e. g. $CoFe_{1.7}Mn_{0.3}O_4$ (CFMO) observed to largely reduce the anisotropy and coercivity while maintaining λ value comparable to that of CFO [26-28]. In addition, substitution of Zn for Co at tetrahedral site A in CFO is also found to reduce the magnetic anisotropy in CFO [29]. Thus, Zn and Mn doped CFO refers as CFMO is a promising magnetic phase to increase ME coupling effect of the composites. Once PCT has the potential piezoelectric/ferroelectric properties, the PCT-CFO/CZFMO composite should be investigated. For comparison, tremendous research has focused on PZT-CFO composites [31-33] in recent years. Although, $(Pb_{0.76}Ca_{0.24})TiO_3$-$CoFe_2O_4$ nanocomposite thin films have been reported by Tang et al. [34], the research for these composites is very rare. Several processing techniques have been used to synthesize multiferroic composites that exhibit magnetoelectric coupling. Zhang et al. prepared NZFO/PZT ceramic by dispersion of nano-sized NZFO ferromagnetic powder into PZT ferroelectric ceramic and showed simultaneous effect of ferromagnetic and ferroelectric at room temperature with good dielectric and magnetic properties [35]. Fawzi et al. studied the ferromagnetic, ferroelectric and magnetoelectric properties of NFO/PLZT composite prepared by double sintering ceramic method [36]. Y. Wang et al. reported good dielectric properties of BST/CFO multiferroic particulate ceramic composite prepared by standard solid state reaction method [37]. In particular metallo-organic decomposition (MOD) wet synthesis of composites is attractive because it provides homogeneous mixing of ferroelectric and ferromagnetic individual precursors at molecular level, low processing temperature to avoid chemical reaction between two phases and to reduce the probability of formation of Fe^{2+} ion, easier composition control and low cost. The decrease in Fe^{2+} concentrations can contribute to an increase in the resistivity and magnetostriction of the ferromagnetic phase. The MOD processed

composites would have higher densities, which may improve the contact between two phases therefore enhance the efficiency of strain transfer from ferromagnetic to piezoelectric component.

2. Experimental Background

❖ Structural Analysis

It is very important to analyze the crystal structure of the prepared samples, as properties of ferrite and ferroelectric constituents depend on the crystalline structure of the sample. The X-ray diffraction of all the samples will be carried out for the structural analysis to confirm the phase formation and crystal structure of the constituent phases. Microstructural analysis of the specimens will be performed by Scanning Electron Microscope (SEM)/ Transmission Electron Microscope (TEM). Compositional analysis will be done by using EDAX. These investigations will be focused on following parameters:

- Multiple Phase identification in composites
- Lattice parameters
- Crystallite Size
- Grain size
- Composition

❖ Electrical & Dielectric Properties

For the measurement of electrical properties, the composite pallets will be electroded with silver paste on both sides. The dc resistivity measurements for all the composite samples will be carried out using two probe method using Kiethley Source meter in the temperature range up to 200^0C. The leakage current of ferroelectric and ferrite phases in composites is primary concern. The leakage should be minimized in order to get better ferroelectric properties. Obtaining high resistivity composites is important for device applications. Microstructure of samples significantly effects the electronic conduction. The relationship between resistivity and temperature is expressed as

$$\rho = \rho_o \exp (E_a/kT)$$

where, ρ is the resistivity at temperature T, ρ_o is the temperature independent constant, k is the Boltzmann constant and E_a is the activation energy for conduction process. The dielectric properties of multiferric magnetoelectric composites are highly influenced by several parameters such as processing technique, composition, grain size, grain distribution and frequency range and temperature. The variation of dielectric constant ($\acute{\varepsilon}$) and the loss tangent

(tanδ) will be measured at room temperature in the frequency range from 1kHz to 1MHz. The dielectric constant will be calculated using the relation

$$\acute{\varepsilon} = \frac{ct}{\varepsilon_0 A}$$

Where, c is the capacitance of the pallet, t is the thickness of the pallet, A is the surface area of the pallet and ε_0 is the permittivity of free space (8.854×10^{-12} F/m). The variation of dielectric constant and loss tangent with temperature at different fixed frequencies will also be studied to understand the dielectric relaxation phenomenon. The dielectric properties will be studied by using Wankerr Impedance Analyzer. Here, the objective of the investigation is to understand the nature of dielectric relaxation mechanisms in composites over temperature and frequency ranges. The variables used in this study are ferromagnetic & ferroelectric phases, composites and substitution impact. Important characteristic parameters of electrical and dielectric studies of composites includes

- Resistivity
- Activation energy
- Conduction mechanism
- Dielectric constant
- Dielectric loss
- Ferroelectric/ferromagnetic phase transition
- Dielectric relaxation mechanisms
- Interfacial polarization

❖ Magnetic Properties

The room temperature magnetization versus applied magnetic field (M-H) hysteresis measurements on $Co_{1-x}Zn_xFe_2O_4$ (CZFO, $0 \leq x \leq 0.8$) ceramic and (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ multiferroic magnetoelectric composite series will be carried out by using Vibrating Samples Magnetometer. The saturation magnetization, coercivity and retentivity will be evaluated from magnetic hysteresis curve for all the samples measured at room temperature. The individual grains of ferrite contribute to these magnetic parameters. The effect of magnetostrictive ferrite constituent on magnetization will be observed from M-H curve. The magnetic measurements would be made on following parameters with varying ferroelectric constituent and substituting Zn & Mn.

- Saturation Magnetization

- Retentivity
- Coercivity
- M-H Hysteresis shape

❖ Ferroelectric Properties

To study ferroelectric ordering in composites, room temperature P-E hysteresis loop will be recorded by using Sawyer-Tower circuit. A comparison of P-F loop parameters such as remanant polarization and saturation polarization will be made with varying ferrite concentration and with co-substitution of Zn and Mn in composites. The results will be correlated with microstructural and phase properties because ferroelectric properties of composites are highly influenced by non-ferroelectric grains surrounding the ferroelectric grains [38-40]. The dielectric and ferroelectric properties can be influenced by domain wall motion. For larger grains, where size of the domain is smaller than the size of the grains, the movement of the domain walls is easier. On the other hand, in small grains, the movement of the domain walls is hindered by the grain boundary. Understanding the domain wall and polarization dynamics of the composites is a crucial component for further development of multiferroic magnetoelectric composite.

❖ Magnetoelectric (ME) coupling measurement

The magnetoelectric (ME) effect in composites is a route for the conversion of energy from magnetic to electric form or vice versa. Therefore tremendous scope of applications in memory devices, magnetic probe for detecting a.c as well as d.c fields and high frequency transducers have been already proposed by various researchers. The linear ME effect was first observed on Cr_2O_3 [41] and theoretically discussed by Landau and Lifshitz [42]. They observed that quite stringent symmetry properties must be satisfied. Spatial and Time symmetry, I and T respectively must be violated while combining the symmetry operation and IT must be valid. In such situation the free energy density F of the system consists of a contribution defined as W = -αH.E, corresponding to H and E coupling via the linear ME susceptibility tensor α. In case of multiferroic materials which do not fulfil the IT symmetry condition, a systematic progression of contribution to the ME effect is obtained from the expansion of the free energy of a material [43].

$$F(E,H) = F_0 - \frac{1}{2}\varepsilon_0\chi_{ij}^{e}E_iE_j - \frac{1}{2}\mu_0\chi_{ij}^{m}H_iH_j - \alpha_{ij}H_iE_j - \frac{\beta_{ijk}}{2}E_iH_jH_k - \frac{\gamma_{ijk}}{2}H_iE_jE_k - \frac{\delta_{ijkl}}{2}E_iE_jH_kH_l \quad (3)$$

Besides, the free energy perturbed terms coupled to binary functions $E^2, H^2 and\, EH$ via linear susceptibility tensor $\chi_{ij}^{e}, \chi_{ij}^{m} and\, \alpha_{ij}$ respectively, recently there has been increasing interest in second order $EH^2 and\ E^2H\ and\ third\, order\, E^2H^2$ effects symbolically represented as $\beta, \gamma, and\, \delta$ effects

respectively. These quantities are very precisely measured by ME SQUID via the electric field induced component of magnetic polarization [44].

$$\mu_0 M_i = -\frac{\partial F}{\partial H_i} = \mu_0 \chi_{ij}^m H_j + \alpha_{ij} E_j + \beta_{jki} E_j H_k + \frac{\gamma_{ijk}}{2} E_j E_k + \delta_{jkl} H_j E_k E_l \quad (4)$$

It consists of external ac and dc electric and magnetic fields, $E = E_{ac}\cos\omega t + E_{dc}$ and H_{dc} and measures the complex first harmonic ac magnetic moment $m(t) = (m' - im'')\cos\omega t$. When the corresponding fields of appropriate amplitudes and direction are applied along the crystal axis, various susceptibility tensor components can be determined. For Polycrystalline sample with volume V the response 'm', allows determining the averaged coupling parameters α, β and δ.

$$m' = (\alpha E_{ac} + \beta E_{ac} H_{dc} + \gamma E_{ac} E_{dc} + 2\delta E_{ac} E_{dc} H_{dc})(V/\mu_0) \quad (5)$$

There is however no really exiting material even roughly satisfies the condition of two simultaneous ferroic transitions.

To measure the direct ME effect $\alpha_E = \frac{\partial E}{\partial H}$ for bulk ME composites, the dynamic change in charge or voltage is usually measure with applying magnetic field to the specimen. In general, there are two measuring modes, active and passive for direct ME effect measurement [45]. In active mode we measure magnetodielectric effect i.e. measurement of capacitive signal charges induced by magnetic field or P-E loop change induced by magnetic field. Therefore, in active mode measurement, the contribution from the magnetoresistive and interfacial capacitive effects must be considered. In passive-mode measurement, no test current or voltage is applied to the sample. Instead, ME voltage induced by a magnetic field applied to the sample is recorded directly. Thus, no contribution from magnetoresistive and interfacial capacitive effects appear in passive mode. The direct ME voltage coefficient will be measured on samples with varying applied dc magnetic field by using dynamic passive mode technique.

3. Experimental Details

The experimental work includes processing of ferrite and ferroelectric compounds and their composites. These specimens will be widely investigated using various experimental techniques to develop an understanding on properties of multiferroic magnetoelectric composites in this specific geometry. The following series of samples will be prepared using metallo-organic decomposition (MOD) processing technique.

a) $Pb_{0.7}Ca_{0.3}TiO_3$ and $Co_{1-x}Zn_xFe_2O_4$ (CZFO, $0 \leq x \leq 0.8$) ceramic powders.

b) (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ multiferroic magnetoelectric composites with, x = 0.2, 0.4, 0.6 and 0.8.

c) The optimized (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ multiferroic magnetoelectric composites with Zn and Mn substitutions/co-substitution.

In the present study, precursors such as Lead-2-ethyl hexanoate $(C_7H_{15}COO)_2Pb$, Calcium-2-ethyl hexanoate $(C_7H_{15}COO)_2Ca$, Cobalt-2-ethyl hexanoate $(C_7H_{15}COO)_2Co$, Zinc-2-ethyl hexanoate $(C_7H_{15}COO)_2Zn$, Iron-3-ethyl hexanoate $(C_7H_{15}COO)_3Fe$ and Manganese-2-ethyl hexanoate $(C_7H_{15}COO)_2Mn$ will be synthesized from starting materials $Pb(NO_3)_2.2H_2O$, $CaCl_2.2H_2O$, $Co(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and $Mn(NO_3)_2.4H_2O$ respectively. The hexanoates so form will be extracted with xylene (solvent) solution. A clear solution of respective hexanoates in xylene will be obtained and these solutions will be kept as metal stock solutions. In all cases nitrate solution will be prepared by dissolving in water and mixed with neutralized 2-ethyl hexanoate solution. The metal-2-ethyl hexanoate either as a top or as a bottom portion of the aqueous solution was extracted with xylene solution.

The chemical reactions involve in precursors synthesis can be described as:-

$$KOH + C_7H_{15}COOH \longrightarrow C_7H_{15}COOK + H_2O$$

$$2C_7H_{15}COOK + Pb(NO_3)_2 \longrightarrow 2KNO_3 + (C_7H_{15}COO)_2Pb$$

$$2C_7H_{15}COOK + CaCl_2 \longrightarrow 2KCl + (C_7H_{15}COO)_2Ca$$

$$2C_7H_{15}COOK + Co(NO_3)_2 \longrightarrow 2KNO_3 + (C_7H_{15}COO)_2Co$$

$$2C_7H_{15}COOK + Zn(NO_3)_2 \longrightarrow 2KNO_3 + (C_7H_{15}COO)_2Co$$

$$3C_7H_{15}COOK + Fe(NO_3)_3 \longrightarrow 3KNO_3 + (C_7H_{15}COO)_3Fe$$

$$2C_7H_{15}COOK + Mn(NO_3)_2 \longrightarrow 2KNO_3 + (C_7H_{15}COO)_2Mn$$

Tetra-n-butyl orthotitanate ($C_{16}H_{36}O_4Ti$) will be used as precursor for Ti content. These stock solutions will be mixed in required molar ratio to prepare $Pb_{0.7}Ca_{0.3}TiO_3$, $Co_{1-x}Zn_xFe_2O_4$ samples and (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ multiferroic magnetoelectric composites. The mixed precursor solution will be magnetically stirred at optimized temperature. Polyethylene glycol (PEG) will be used as surfactant. The resultant solution will be subsequently dried at optimize temperature. The dried powder will sintered for crystallization. Now weighted amount of both powder phases will be taken and homogenized these powders by grinding with pastle-mortar. The mixture will again be sintered at higher temperature to produce composites. Now the powder will be pressed into pallets by using hydraulic press and finally pallets will sintered at further higher temperature. Similar steps will be followed for synthesizing all the samples. The structural, compositional analysis, magnetic, ferroelectric, electronic, dielectric and magnetoelectric characterization of these

samples will be carried out using XRD, SEM, EDAX, VSM, P-E set up, source meter, impedance analyzer and ME measurement set up.

4. Objectives

The literature survey reveals that no report is available on metallo-organic decomposition (MOD) synthesized PCT-CFO/CZFMO magnetoelectric composites. In the present research work we have planned to synthesize (1-x)$Pb_{0.7}Ca_{0.3}TiO_3$ – (x)$CoFe_2O_4$ and with Zn, Mn substituted composites by metallo-organic decomposition technique. The main objective of the plan of research work is to carry out a systematic investigation on $(Pb_{0.7}Ca_{0.3}TiO_3)_{1-x}$ – $(CoFe_2O_4)_x$ and with Zn, Mn substituted composites. Their structural, compositional, dielectric, magnetic, ferroelectric, and magnetoelectric properties will be investigated. Moreover, it will be very interesting to study ferromagnetic concentration dependent ferroelectric properties of these composites. Further, we believe that the ME coupling effect in (1-x)$Pb_{0.7}Ca_{0.3}TiO_3$ – (x)$CoFe_2O_4$ composites will be enhanced by co-substituting with Zn and Mn.

5. Plane of work with work done till date

1. To synthesize $Pb_{0.7}Ca_{0.3}TiO_3$ (PCT) and $Co_{1-x}Zn_xFe_2O_4$ (CZFO, $0 \leq x \leq 0.8$) ceramic powders by metallo-organic decomposition (MOD) wet chemical technique. The structural studies of PCT powder will be carried out to confirm the phase formation. The concentration of Zn in CZFO ceramic powders will be optimized by their structural and magnetic properties analysis. The microstructural and dielectric properties of CZFO will be investigated in detail for comparison.
2. To prepare (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$– x$CoFe_2O_4$ (PCT-CFO) multiferroic magnetoelectric composites with, x = 0.2, 0.4, 0.6, 0.8 and to establish an optimum molar concentration of magnetic phase by systematic investigation.
3. To synthesize the optimized molar (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$– (x) $CoFe_2O_4$ (PCT-CFO) multiferroic magnetoelectric composites with Zn and Mn substitutions as well as with co-substitution.
4. To understand the compositional effect of ferromagnetic/ferroelectric phases and Zn and Mn substitution on (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$– (x) $CoFe_2O_4$ (PCT-CFO) multiferroic magnetoelectric composites through extensive investigation on their structural, dielectric, magnetic, ferroelectric and magnetoelectric coupling properties.

The above investigations will fulfil the scarcity of available reports on properties of PCT-CFO multiferroic magnetoelectric composite to establish their possible device applications.

❖ Investigation Completed

- ✓ The structural properties of $Pb_{0.7}Ca_{0.3}TiO_3$ ceramic powder have been studied.
- ✓ The structural, microstructural, dielectric, and magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ (CZFO, $0 \leq x \leq 0.8$) ferrites have been studied and $x = 0.4$ is the optimized concentration of Zn for better ferromagnetic properties of $Co_{1-x}Zn_xFe_2O_4$.
- ✓ The structural, microstructural, dielectric, electronic, magnetic, ferroelectric and magnetoelectric studies on (1-x) $Pb_{0.7}Ca_{0.3}TiO_3$ – (x) $CoFe_2O_4$ multiferroic magnetoelectric composite series have been completed. 20 mol% of $CoFe_2O_4$ has been optimized for better magnetoelectric coupling effect.
- ✓ The structural and magnetic properties of $Co_{0.6}Zn_{0.4}Fe_2O_4$, $CoFe_{1.8}Mn_{0.2}O_4$ and $Co_{0.6}Zn_{0.4}Fe_{1.8}Mn_{0.2}O_4$ specimens have been studied.

❖ Investigation under progress

Detail investigation on structural, dielectric, electronic, magnetic, ferroelectric and magnetoelectric properties of following three Mn and Zn substituted composites is under progress.

i) (0.8) $Pb_{0.7}Ca_{0.3}TiO_3$ – (0.2) $Co_{0.6}Zn_{0.4}Fe_2O_4$

ii) (0.8) $Pb_{0.7}Ca_{0.3}TiO_3$ – (0.2) $CoFe_{1.8}Mn_{0.2}O_4$

iii) (0.8) $Pb_{0.7}Ca_{0.3}TiO_3$ – (0.2) $Co_{0.6}Zn_{0.4}Fe_{1.8}Mn_{0.2}O_4$

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